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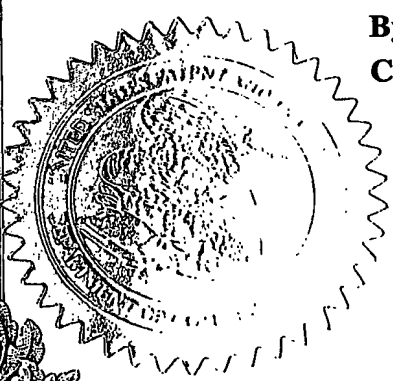
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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under
37 C.F.R. § 1.53(c).

TITLE: LANTHANIDE(III)-DOPED NANOPARTICLES AND THEIR APPLICATIONS

Inventor(s)/Applicant(s):

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Last	First	MI	City, State or Foreign Country and City

☒   18 pages of specification are enclosed.

☒   Small entity status is claimed for this application.

☒   Provisional Filing Fee Amount:
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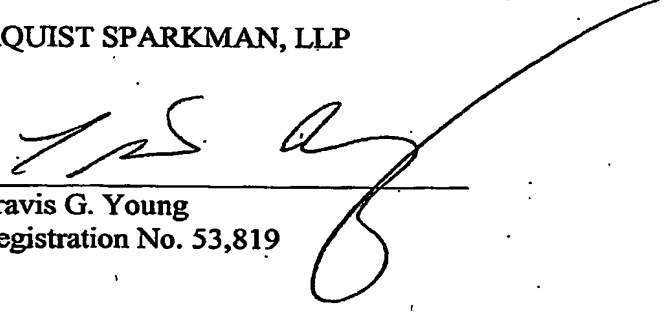
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LANTHANIDE(III)-DOPED NANOPARTICLES AND THEIR APPLICATIONS

5   Frank C.J.M. van Veggel, Gerald A. Hebbink, Jan W. Stouwdam,
University of Twente, Lab. of Supramolecular Chemistry and Technology and
MESA+ Research Institute, Enschede, The Netherlands.

Luminescent nanoparticles currently attract a great deal of interest as
components in LEDs, displays, biological essays, optoelectronic devices with
10   nanometer dimensions, and as light source in zero-threshold lasers. Our interest is
in particular to use these materials in (polymer-based) lasers and optical amplifiers
and integrate them with polymer-based components for telecommunication. In
particular the optical window between 1300 and 1600 nm is important. Here we
report the synthesis and optical properties of $LaPO_4$, $GdPO_4$, YPO_4, $LuPO_4$, and
15   LaF_3 doped with Er^{3+}, Nd^{3+}, Pr^{3+} that emit in the near infrared. The synthesis
followed a wet chemical approach, which led to redispersable nanoparticle with
diameters in the range of 5-8 nm. The Er^{3+}-doped material shows luminescence
around 1550 nm with lifetimes up to 2.3 ms. The Nd^{3+}-doped material shows the
typical lines at 880, 1069, and 1330 nm, with lifetimes in 100-150 μs range. The
20   Pr^{3+}-doped material has various emissions in the visible region, but also an
emission between 1400 and 1500 nm, with a lifetime of several μs. The combined
emission of these three lanthanide ions cover the complete range of 1300 to 1600
nm, thus giving the potential of a compact broad-band polymer-based optical
amplifier. The processability of these materials was proven by incorporating them
25   in a thin PMMA layer on quartz and measuring the optical properties, which were
not significantly altered.

Summary of Nanoparticle Proposal

Lanthanides are a series of ('rare earth') elements in the periodic table (57-71) including:
(La), Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

Nd^{3+} (1330 nm), Er^{3+} (1550 nm) emit in the telecommunications window, and with Yb^{3+} (980 nm), Ho^{3+} (1450 nm) and Pr^{3+} (1330, 1450 nm), emit in the near infrared (800-1600 nm).

Radio	microwave	INFRARED	VISIBLE	UV	X-ray	γ-ray
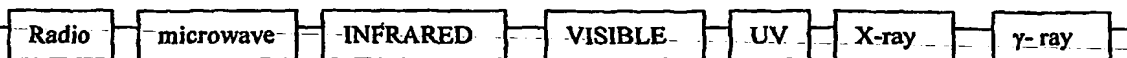
The proposal is to create nanoparticles from a material that is a semiconductor (Al_2S_3, Ga_2O_3, In_2O_3) and integrated or "doped" with a Ln^{3+}. These semiconductors are both electroluminescent and photoluminescent.

The emission of infrared from the lanthanide ion is the result of an energy transfer to the ion from a stimulated sensitizer (triphenylene, fluorescein, dansyl, coumarine, lissamine), which is in close proximity to the Ln^{3+}.

To improve the long-term stability of the ion, an inorganic matrix will be used as an insulator (LaF_3, $LaPO_4$) which won't quench the emission and is photoluminescent. These molecules meet the requirement that (a nanoparticle with application to polymer-based devices):
1. Ln^{3+}-doped material should be processable
2. Size should be nanometer range to avoid scattering
3. High luminescent yield
4. Robust under constant excitation

The inorganic core is surrounded by the inorganic insulator and then by an organic layer with hole/energy conduction properties, water solubility, terminal reactive groups for labeling, shields Ln^{3+} from solvent. Hole conductors include aromatic amines; electron conductors include oxadiazoles, 1,2,4-triazoles, 1,3,5-triazines and quinoxalines.

*Electroluminescence has not been demonstrated with Ln^{3+}-doped semiconductor nanoparticles.

Research Proposal

Introduction:

Materials on a nanoscale attract much attention these days because of fundamental reasons as well as potential application in nanosized devices. Nanosized materials often exhibit fundamentally different properties compared their bulk counterparts, because of quantum phenomena. The nanosized devices are the next step in the on-going strive for faster performance of chips, higher data storage capacities of hard drives, faster telecommunication devices through integration of components on chips, etc. The proposal focuses on a hybrid approach to make new optical materials that emit in the near-infrared (800-1600 nm), with potential application in polymer-based optical amplifiers and lasers, light-emitting diodes, and biolabels.

Rational of the scientific approach:

The approach follows a hybrid approach in the sense that the nanoparticle is based on an inorganic material in which the luminescent material is doped and that it is stabilized by a monolayer of surfactant-like molecules, which also guarantees processability. The luminescent trivalent lanthanide ions are chosen as luminescent source because they have the appropriate optical transitions in the near-infrared. In addition, these luminescent Ln^{3+} ions are known for their robustness under laser excitation and have shown excellent optical properties in bulk inorganic matrices. The stabilizing organic monolayer allows the introduction of specific functionality such as hole- and electron-conducting properties, water solubility, terminal reactive groups for labeling, etc (see the proposal section for more details).

Progress report:

The concept of sensitized near-infrared emission of trivalent lanthanide ions that we have been following over the last 10 years at the University of Twente (The Netherlands) is schematically depicted in Figure 1. The sensitizer is excited to its first singlet excited state, after which intersystem crossing populates the triplet state. The triplet is generally the state from which energy transfer to the lanthanide ion takes place. The process of intersystem crossing is enhanced by the presence of the Ln^{3+} ion, allowing the use of (fluorescent) sensitizers with low inherent triplet state populations. Effective harvesting of the excitation light is usually guaranteed by using highly colored chromophores.
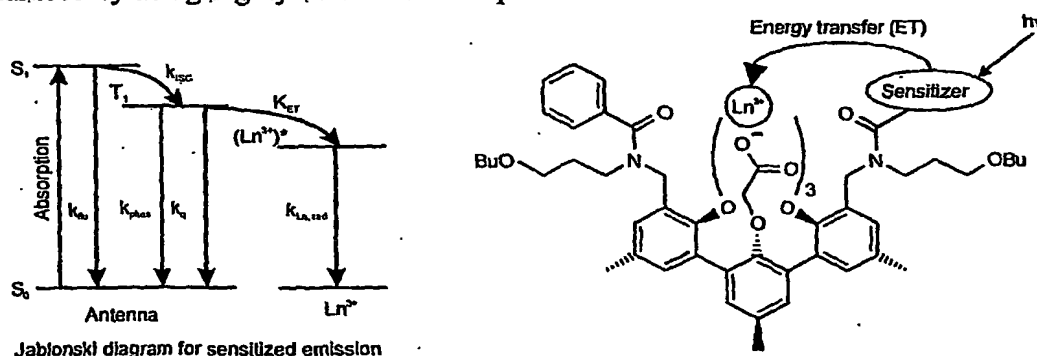

Jablonski diagram for sensitized emission

Figure 1 (Jabonski diagram + terphenyl-based polydentate ligand with covalently bound sensitizer)

A flexible synthesis route based on the terphenyl moiety as building block has been designed, which allows the introduction of carboxyacetate ligands and amide groups in addition to attachment of the sensitizer (Figure 1). The polydentate ligand effectively shields the Ln^{3+} ion from solvent. In particular water and methanol have to be stripped from the Ln^{3+} ion because they are efficient quenchers through their OH groups. The covalent attachment brings the sensitizer in relatively close proximity, which is a prerequisite for efficient energy transfer. Sensitized emission of Nd^{3+} (880, 1060, and 1330 nm), Yb^{3+} (980 nm), and Er^{3+} (1550) has been demonstrated with a variety of sensitizers such as triphenylene, fluorescein, dansyl, coumarin, and lissamine. In general the energy transfer of the excited sensitizer to the Ln^{3+} ion is from the triplet state, but we and others have accumulated evidence over the last few years that certain sensitizers show energy transfer from the singlet excited state. So far, lissamine and dansyl have been identified as sensitizers that transfer through the singlet excited state. This may be due to the presence of nitrogen atoms with their quadrupoles in their chromophoric part. Our work on this issue will appear in *ChemPhysChem*.[ref]

The long-term stability of the sensitizers is an inherent weak point when organic chromophores are being used. We were the first to show that sensitized emission of Nd^{3+} and Yb^{3+} can be achieved with organo-d-metal complexes such as $Ru(bipy)_3$ and ferrocene, which were covalently attached in a similar fashion as described above.

From all our detailed photophysical studies it has become clear that usually the rate of energy transfer from the excited sensitizer to the Ln^{3+} ion is (much) lower than the intersystem crossing rate. This is mainly caused by the distance between the sensitizer and the Ln^{3+} ion. Ternary Ln^{3+} complexes with the sensitizer directly coordinated to the Ln^{3+} ion have solved this inefficiency.

A problem that remains is the very low overall quantum yields of sensitized emission, i.e. quantum yields up to only a few percent in the case of Nd^{3+} and Yb^{3+}, but much lower for Er^{3+} (<0.1%). The non-radiative decay pathways that deactivate the excited Ln^{3+} ion are the reason for this. Many deactivation pathways, involving for instance CH groups of the ligand, are present. This can be improved by incorporating CD groups, but the effect is only an increase of the quantum yield by a factor of 2-2.5.

In collaboration with Prof. Friend (Cambridge, UK) we have shown that these complexes emit near-infrared light in polymer-based light-emitting diodes and that the sensitizer is essential. It is, however, my believe that the "organic approach" is bound to fail when long-term stability is crucial, which will be the case in polymer-based devices such as optical amplifier, lasers, and light-emitting diodes. On the other hand, it may serve nicely in (immuno-)assays.

One solution to the problems described above is the use of an inorganic matrix to host the luminescent Ln^{3+} ions. A number of inorganic matrices are available with LaF_3 potentially the best "low-phonon" matrix because of its low vibrations (300-350 cm^{-1}), in other words: the matrix is expected to hardly quench the excited Ln^{3+}. A few conditions have to be met before these materials can be applied in polymer-based devices. The Ln^{3+}-doped material should be processable, its particle size should be in the nanometer range to avoid scattering, it should have high luminescent quantum yield, and it should be very robust under constant excitation. We have been the first to show that these criteria can be met by Ln^{3+}-doped nanosized materials based on $LaPO_4$ and LaF_3 as host that emit in the near-infrared ($LaPO_4$: *Adv. Mat.* and LaF_3: *Nano Letters*).[ref] Stable and processable materials have been obtained through the use of a stabilizing monolayer of coordinated surfactant-type molecules. These molecules regulate nucleation and growth of the nanoparticle and prevent agglomeration. Efficient emission of Nd^{3+}, Yb^{3+}, Er^{3+}, Pr^{3+} (1400-1500 nm), and Ho^{3+} (1425-1475 nm) has been obtained thus covering the whole range

of 1300 to 1600 nm, making broad-band amplifiers potentially possible. Current standard telecommunication windows are at 1330 and 1550 nm, but the window around 1450 nm is likely to become available as well due to the current progress on low-loss fibers. The estimated quantum yields of Nd^{3+} and Er^{3+} are in the range of 15%. The Nd^{3+}-based material is currently being tested in microring resonators in a collaboration with Dr. Driessen (University of Twente, NL). Preliminary experiments showed spontaneous amplified emission. Robustness of the material under constant excitation for more than 20 hours has already been demonstrated! Measurements of the lifetime of the excited Ln^{3+} ion showed that not a single value was present but a range of values. Detailed studies showed that the quenching by the solvent is present, which has a clear distance dependence.[ref] In order to take this distance dependence into account, a physical model based on 10 shells for the nanoparticle has been proposed (Equation 1). This simple model gives very good fits (see Figure 2). Equation 1 has basically two parameters: one is the decay rate of the Ln^{3+} ions k_R and the other is the quenching of the Ln^{3+} ions by surface quenchers, giving the decay rate for shell i. The parameter k_R is the radiative life time in the absence of surface quenchers and the constant C depends on the individual luminescent Ln^{3+} ion, the size and size distribution of the nanoparticles, and the strength of the quenching. The term $f_{q,i}$ gives the distance between the shell i and all the quenchers surrounding the particle. The required integrations have been done in Excel.[TM] For more details I would like to refer to two recent papers by the applicant and co-workers.[ref]

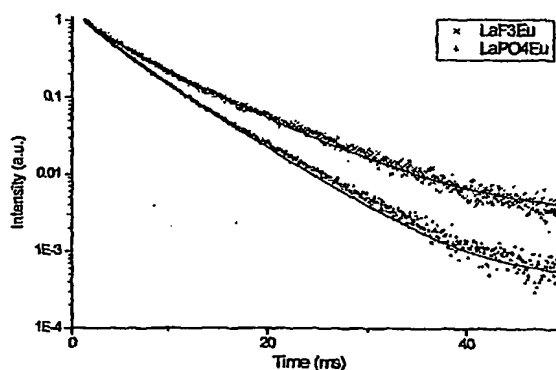$$I_t = I_0 \sum_{i=1}^{10} \frac{1}{10} e^{-k_i t}; k_i = \frac{1}{\tau_i} = k_R + C \times f_q(r)$$

(Eq 1)

Figure 2 (decay curve + fit)

Some preliminary results have been obtained with semi-conductor nanoparticles based on Eu^{3+}-doped Al_2S_3. A precursor complex of $AlCl_3$ and trioctylphophine oxide (TOPO) was prepared that was reacted in hot trioctylphophine (250 °C) with sulfur. Doping was done by addition of $EuCl_3$. The excitation spectra of in-situ prepared material clearly shows energy transfer from Al_2S_3 to Eu^{3+}, giving the characteristic red emission of Eu^{3+}. There is still an appreciable amount of emission from Al_2S_3, so many improvements have to be made here.

These investigations by 1-PhD I still have in The Netherlands on the Ln^{3+}-doped nanoparticles will come to a close in approximately one year including writing a thesis, leaving many questions unresolved.

Proposal:
A systematic investigation is proposed on Ln^{3+}-doped nanoparticles based on inorganic insulators and semi-conductors with a stabilizing (functional) organic monolayer. The following questions and issues will be addressed:
1) The synthesis and purification procedures have to be optimized to increase the monodispersity of the doped nanoparticles. Once this is achieved, the photophysical measurements will give much more insight in the effect of surface quenchers, the effect of the concentration of the luminescent Ln^{3+} ion, the effect of co-doping with a sensitizer (a well known sensitizer of Er^{3+} is Yb^{3+} which has a relatively broad and intense absorption around 940 nm). These data will put the physical model to a stricter test and lead to a deeper insight of the system.
2) Methods have to be developed to produce core-shell particles in the sense that the doped inorganic nanoparticle is covered by a layer of (another) inorganic material to which the stabilizing monolayer is bound. This core will place the luminescent Ln^{3+} ions further away from surface quenchers thus increasing the life time. To obtain a single life time for all luminescent Ln^{3+} ions in the nanoparticle is important for any device optimization in the future.
3) Surface modification is another important objective. It will lead to materials with increased stability, and it will allow the introduction of functional terminal groups for covalent anchoring to a polymer or sol-gel matrix. The use of these doped nanoparticles in a sol-gel as matrix will avoid the problem of remaining OH groups and will give very wear-resistant materials. Surface modification will also produce materials that are water soluble, an obvious requirement for biolabels. The Ln^{3+} ions that emit in the near-infrared are attractive because tissue is relatively transparent to this radiation thus allowing measurements with the excitation and detection outside the body.[ref] Two general approaches are possible: ligand exchange after synthesis of the nanoparticle or chemical modification of the ligands.
4) The development of Ln^{3+}-doped nanoparticles based on semi-conductors that have efficient emission in the near-infrared. The advantage of a semi-conductor as host is that electrical excitation will be possible in devices such as (polymer-based) light-emitting diodes. This is not possible with nanoparticles based on insulators such as $LaPO_4$ and LaF_3. To date, there are no examples of these materials in the literature, although a number of publication hint at it.[refs] Recently, Meijerink et al. have published a paper stating that so far all attempts to incorporate Ln^{3+} in nanoparticles of CdSe and thelike have failed.[ref] Possibly two factors are involved in the failures. One is a charge mismatch and the other is a lattice mismatch. Materials with a stoichiometry of M_2X_3 are much better candidates (vide infra). Materials that will be tested initially include: Al_2S_3, In_2O_3, Ga_2O_3, Ga_2S_3, Ga_2Se_3, Ga_2Te_3, $(\Box\Box)In_2Te_3$, etc. It will be important to establish the bandgap of the nanoparticle, which will determine if energy transfer to the Ln^{3+} ion is possible. Knowing that Al_2S_3 (the bandgap of bulk Al_2S_3 is 4.2 eV)[ref] can excite Eu^{3+} makes it likely that also Ln^{3+} ions that emit in the near-infrared can be excited. The bandgap of $\Box In_2Te_3$ and $\Box In_2Te_3$ are 1.1 and 1.0 eV, respectively,[ref] which is only allows Er^{3+} to be excited.

5) One of the crucial issues in light-emitting diodes is the recombination of injected holes and electrons into an exciton. The exciton can then radiatively decay to the ground state giving the characteristic emission of that compound/material. In the case of Ln^{3+}-doped semi-conductor nanoparticles the holes and electrons have to cross the stabilizing organic monolayer. In order to facilitate this process hole- and electron-conducting moieties have to be introduced into this organic monolayer (schematically depicted in Figure 3).
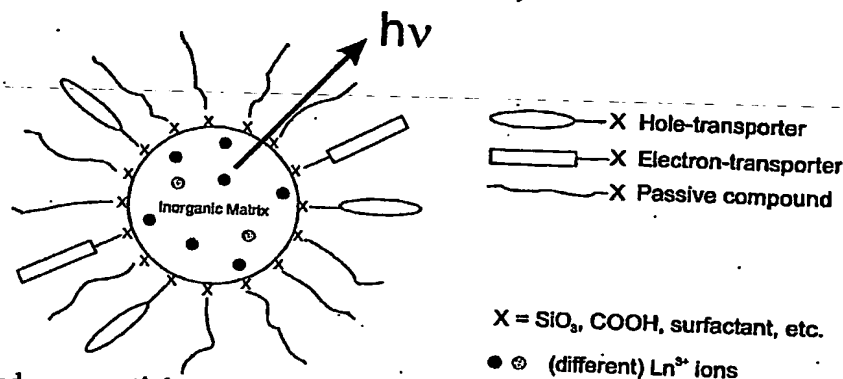

Figure 3 (Doped nanoparticle with hole- and electron-conductors in the stabilizing monolayer)

A number of potential candidates are available based on recent work on polymer and organic light-emitting diodes. Hole conductors are usually aromatic amines, because they have low oxidation potentials and high hole mobilities. An often applied compound is TPD, tetraphenyl diaminobiphenyl. This type of compound is also applied in photocopy machines and laser printers. As electron transporter oxadiazoles, 1,2,4-triazoles, 1,3,5-triazines, and quinoxalines are possible candidates.[ref] Oligomers like oligothiophenes and oligopyrroles are also alternatives. Part of their attractiveness stems from the fact that their synthetic chemistry is quite advanced.[ref] This should make it possible to match oxidation and reduction potentials of the various components. Synthetic strategies will be developed to functionalize these compounds substituents that coordinate to the surface of the nanoparticle.

6) The theoretical work has to be extended for a deeper insight. So far all processes within the nanoparticle are treated with one parameter (i.e. $k_R = 1/\square_R$ in equation 1, so $\square_R$ is not necessarily the radiative life time, but includes quenching processes within the nanoparticle). The physical model has to include:

1) energy migration between the Ln^{3+} ions;

2) energy transfer between a co-dopant and the dopant (for instance for the combination of Yb^{3+} and Er^{3+});

3) quenching sites within the nanoparticle;

4) cross relaxation processes (these involve two excited Ln^{3+} ions whereby one decays to the ground state and the other changes to a higher excited state). This is in particular important for Er^{3+}-doped materials because Er^{3+} has a radiative life time up to 20 ms, thus giving these processes ample time to occur;

5) excited state absorption (ESA), which may occurs when high excitation powers are being applied. Also here the life time of the luminescent Ln^{3+} ion is relevant; the longer the life time the higher the chance that ESA occurs.

The processes 3, 4, and 5 are losses of excitation energy and therefore have to be avoided/minimized.

Ln^{3+}-doped nanoparticles that emit in the near-infrared, stabilized by a self-assembled monolayer of organic ligands

Execution of the proposed research will lead to new hybrid optical materials based on processable nanoparticles that are doped with luminescent Ln^{3+} ions, with an emphasis of luminescence in the near-infrared. The near-infrared luminescence of Nd^{3+} (1330 nm) and Er^{3+} (1550 nm) covers two important telecommunication windows. In addition, those Ln^{3+} ions that emit in the near-infrared, Nd^{3+}, Er^{3+}, Yb^{3+} (980 nm), Ho^{3+} (1450 nm), and Pr^{3+} (1330 and 1450 nm), may also lead to unique biolabels. These days nanoparticles attract a lot of attention because of their different properties as compared to their bulk counterparts and because of their potential applications. This research will be a major theme of a broad-based program on self-assembled materials for optical applications, as part of my Canadian Research Chair on supramolecular photonic materials. The long-term objectives are the synthesis and solid (photo-)physical characterization of these new materials, followed by proof-of-principle of their applicability. This research will benefit heavily from my ongoing explorations on the luminescent properties of Ln^{3+} complexes and their potential applications (25 refereed publications since 1997).

Processability and size control of the nanoparticles will be ensured by ligands with groups that form a self-assembled monolayer through coordination to the surface of the nanoparticles. As matrix both insulators, e.g. LaPO$_4$ and LaF$_3$, and semiconductors, e.g. Al$_2$S$_3$, Ga$_2$O$_3$, and In$_2$O$_3$, will be exploited. In addition to optical excitation (photoluminescent, PL), the semiconductor-based luminescent materials have the potential of electrical excitation (electroluminescence, EL) in e.g. polymer-based light-emitting diodes (LEDs), with the stabilized nanoparticles as dopant. So far EL has not been demonstrated with Ln^{3+}-doped semiconductor nanoparticles because of the lack of efficient luminescent materials. These new materials may find their way in polymer-based amplifiers and lasers (light sources) as components of integrated optics, operating in the telecommunication windows. Preliminary results on efficient PL in the near-infrared of Ln^{3+}-doped insulators has recently been shown by us (for initial results on LaF$_3$: *Nano Letters*, 2002, 7, 733-737; LaPO$_4$: *Adv. Mat.* in press).

A systematic investigation is anticipated that deals with the following issues. Simple, preferably one-pot, synthesis routes will be developed by varying the matrix, the stabilizing ligand, the concentration of the (co-)dopant, etc. Effective synthesis routes will be established to make core-shell particles, i.e. particles with a luminescent core surrounded by a passive inorganic layer. Surface reactions and ligand exchange reactions on the self-assembled monolayers will be investigated to affect their stability and solubility. New functional ligands will be synthesized, i.e. ligands with moieties that e.g. facilitate electron- and hole-transport in EL devices beside their group that coordinates to the surface of the nanoparticle. Extensive PL studies will be conducted to establish the emissive properties, life time, quantum yields, etc, for which the necessary infrastructure is in-house. These PL studies will provide the data for a physical model that describes the luminescent behavior in great detail. This is needed because our initial studies have shown that the materials have a distribution of life times and hence quantum yields. This distribution is caused by the fact that the Ln^{3+} are randomly distributed over the nanoparticles and as a result some are affected by surface quenchers. In order to avoid this, core-shell particles are pursued. The Ln^{3+}-doped semiconductor nanoparticles will be tested in polymer-based LEDs. Basic devices can be made in our own laboratories and the most

promising will be doped in more advanced devices in a collaboration with Prof. Friend (Cambridge, UK).

The nanoparticle-based biolabels need of course a stabilizing shell of ligands that make them water soluble. This can be done by either reaction at the terminus of the stabilizing ligands or by ligand exchange reactions. Via these routes also reactive moieties can be introduced for the final labeling of cells, DNA, proteins, etc.

Applications of Research

1) Ln3+ doped nanoparticles based on insulators. Application are in the field of polymer-based optical amplifiers and laser with optical pumping of the medium. Advantages are cheap production and ease of integration with polymer-based devices, such as splitter, switches, etc.

2) Ln3+ doped nanoparticles based on semiconductors. Applications also in the field of polymer-based optical amplifiers and laser, BUT with electrical pumping of the medium. This is very much desired for it is probably the easiest and cheapest way to pump.

3) Ln3+ doped nanoparticles as biolabels. Advantages are non-overlapping excitation AND emission in the near-infrared, where tissue is relatively transparent. This potentially makes excitation and emission outside the body possible, thus being a non-invasive analysis after the injection of the labels.

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Lanthanide(III)-Doped Nanoparticles That Emit in the Near-Infrared**

By *Gerald A. Hebbink, Jan W. Stouwdam, David N. Reinhoudt*, and *Frank C. J. M. van Veggel**

Luminescent nanoparticles attract a great deal of interest as components in light-emitting diodes (LEDs),[1] displays,[2] biological assays,[3] optoelectronic devices with nanometer dimensions,[4] and as a light source in zero-threshold lasers.[5] The materials employed are for instance semiconductor particles such as cadmium selenide[6] and indium arsenide,[7] and lanthanide(III)-doped oxide materials. The latter are of special interest due to their applicability in optical amplifiers and lasers.[8,9]

Lanthanide(III)-doped nanoparticles have been reported previously,[10] following procedures with high temperatures or bombarding experiments,[11] but these methods generally suffer from products with a low processability. Only a small

[*] Dr. F. C. J. M. van Veggel, G. A. Hebbink, J. W. Stouwdam, Prof. D. N. Reinhoudt
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number of redispersible nanoparticles have been reported that are doped with lanthanide(III) ions such as Eu^{3+} and Tb^{3+}, which emit visible light.[12–15] Processable nanoparticles doped with near-infrared (NIR) emitting lanthanide(III) would be of particular interest as the active material in polymer-based telecommunication components, polymer-based lasers, polymer displays, and polymer LEDs. An advantage of nanoparticles over organic complexes[16] is that the lanthanide ion is embedded in an inorganic matrix, yielding long luminescence lifetimes and high quantum efficiencies.

Here, we report the first redispersible lanthanide-doped nanoparticles that emit in the NIR and we show that these particles can easily be incorporated in polymer materials.

The colloids doped with the NIR-emitting Pr^{3+}, Nd^{3+}, Er^{3+}, Yb^{3+}, and Er^{3+} co-doped with Yb^{3+} ions were prepared according to a literature procedure.[13] More details can be found in the Experimental section. The particles were characterized by transmission electron microscopy (TEM); a typical image is shown of the $LaPO_4$:Pr particles in Figure 1.

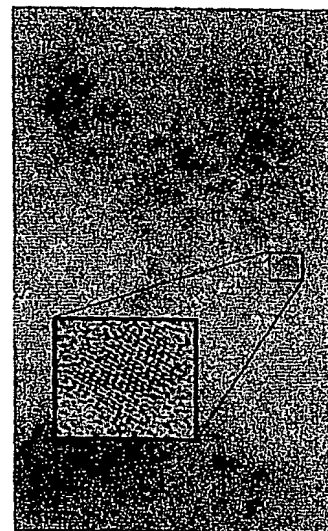Fig. 1. TEM image of $LaPO_4$:Pr particles on a carbon-coated grid. The inset shows the high crystallinity of the particles

The picture shows that the particles are not ideally spherical and that the average size of the particles is about 5–7 nm.[17] The inset shows a magnification of some particles to illustrate the high crystallinity. The particles seem to cluster on the TEM grid but in solution they are present as single particles. This has been measured before with small-angle X-ray scattering.[12]

The elemental composition of the colloidal powders was determined by elemental analyses and by X-ray fluorescence (XRF), the latter being an excellent technique to distinguish between the different lanthanide ions. The elemental compositions obtained from elemental analyses and XRF are presented in Table 1. The molar ratio La^{3+}/Ln^{3+} is in all cases about 19:1, as was applied in the synthesis. Furthermore, the

Table 1. Elemental composition [wt.-%] of LaPO₄:Ln³⁺ particles.

	La [a]	Ln [a]	P [a]	C [b]	N [b]	H [b]
LaPO₄:Nd	41.97	2.42	12.19	6.33	1.01	2.16
LaPO₄:Er	41.80	2.36	12.56	5.57	1.20	2.63
LaPO₄:Pr	43.30	2.35	12.52	6.30	1.01	2.17

[a] XRF. [b] Elemental analysis.

phosphorus content is higher than needed stoichiometrically for LnPO₄; the excess in phosphorus is present as phosphates and phosphate esters bound to the surface of the particles. The remaining 10 % is organic material, mainly surface alkyl groups, tetramethylammonium salts, and traces of water. The presence of the organic groups was confirmed by ^{1}H NMR spectroscopy, where broadened signals (3.3 ppm for NMe₄⁺ and 1.2 and 0.9 ppm for surface-bound ethylhexyl moieties) were found for these compounds. The line broadening is consistent with the surface binding of the organic groups to the particles.

The emission and excitation spectra in the visible region of the Pr³⁺-doped colloids are depicted in Figure 2. The emission spectrum in the visible was obtained by exciting the sample at
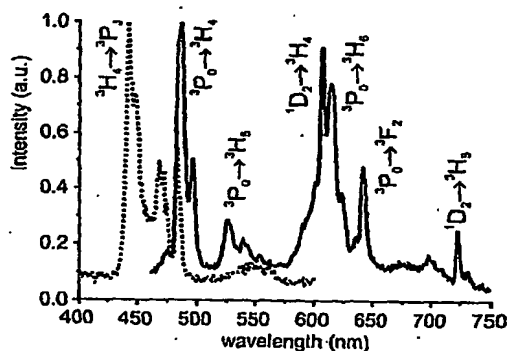
Fig. 2. Excitation (λ_{em} = 730 nm) and emission (λ_{exc} = 442 nm) spectra of LaPO₄:Pr in CD₃OD ([Pr³⁺] ~ 10⁻³ M).

Fig. 3. Emission spectra in the NIR of LaPO₄:Ln in CD₃OD at 10⁻³ M with Ln³⁺ = Pr³⁺ (λ_{exc} = 476 nm, panel A), Nd³⁺ (λ_{exc} = 514 nm, panel B), and Er³⁺ (λ_{exc} = 488 nm, panel C).

442 nm. The strongest emission peaks were observed around 490 nm, 530 nm, and 620 nm, attributed to the $^3P_0 \rightarrow ^3H_4$, $^3P_0 \rightarrow ^3H_5$, and $^1D_2 \rightarrow ^3H_4$ transitions, respectively. A number of excitation peaks were observed between 460 and 490 nm (measured by collecting the emission at 730 nm), attributed to the $^3H_4 \rightarrow ^3P_J$ (J=2,1,0), and the $^3H_4 \rightarrow ^1D_2$ transitions.

The emission spectrum of LaPO₄:Pr in the NIR, obtained by exciting the sample with an Ar⁺ ion laser at 476 nm, was collected with a Ge detector (above 850 nm) or a photomultiplier tube (PMT) (AgOCs) for the part below 850 nm. This NIR emission spectrum (A), together with the emission spectra of LaPO₄:Nd (B) and LaPO₄:Er (C) are depicted in Figure 3. The latter two were collected by exciting with the 514 nm and the 488 nm Ar⁺ ion line, respectively. The NIR spectrum of LaPO₄:Pr (A) exhibits a number of transitions between 800 and 1100 nm of the $^1D_2 \rightarrow ^3F_J$ (J=2, 3, 4) transitions and a broad peak between 1400 nm and 1550 nm attrib-

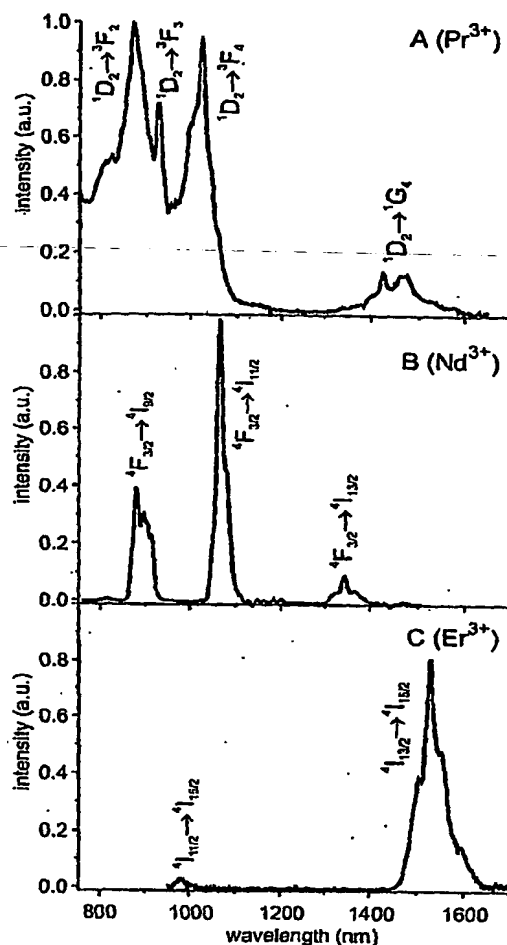uted to the $^1D_2 \rightarrow ^1G_4$ transition. The emission spectra of LaPO₄:Nd (B) and LaPO₄:Er (C) show the typical Nd³⁺ transitions at 880, 1060, and 1330 nm ($^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, and $^4F_{3/2} \rightarrow ^4I_{13/2}$, respectively) and Er³⁺ transitions at 980 nm ($^4I_{11/2} \rightarrow ^4I_{15/2}$) and 1550 nm ($^4I_{13/2} \rightarrow ^4I_{15/2}$). By using these lanthanide(III) ions, the spectral region from 1300 nm to 1600 nm, which is of particular interest for telecommunications applications,[18] can be covered completely. The Yb³⁺/Er³⁺ ion combination is of great importance in Er³⁺-doped optical amplifiers where Er³⁺ is pumped indirectly via Yb³⁺, which has a 10 times higher absorption cross section and a much broader peak at 980 nm than Er³⁺.[19] Er³⁺ luminescence at 1536 nm was observed in LaPO₄ particles that were doped with 5 % Er³⁺ and 5 % Yb³⁺ upon excitation of the charge-transfer band around 250 nm that initially leads to excited Yb³⁺ ions.[20] The particles doped with only Er³⁺ did not exhibit this broad excitation peak, which proves that upon excita-

tion of Yb^{3+} via the charge-transfer band the energy is transferred to the Er^{3+} centers. Particles doped with Yb^{3+} alone had the same charge-transfer band at 250 nm, but of course only Yb^{3+}-based luminescence at 980 nm was observed there.

Luminescence lifetimes were determined by collecting the decay of the luminescence intensity of the strongest intensities of the luminescence spectra after excitation with the same Ar^+ ion laser lines as above. Two effects were studied, i.e., the role of the solvent in luminescence quenching and the role of the ion concentration on the luminescence. The first effect was measured on the Nd^{3+}-doped particles, the latter effect was measured on particles doped with varying Er^{3+} concentration. The lifetimes of the Nd^{3+}-doped particles were determined in solvents with varying deuteration grade: methanol, methanol-d_1, and methanol-d_4, because the higher the deuteration grade, the lower the quenching will be. The obtained decay trace is clearly not mono-exponential. Because the strongest quenching groups are located at the surface of the particles, a fitting procedure was developed that takes into account the distance between the surface of a particle and the luminescent ions in the particles. A particle was subdivided into 10 shells with equal volume, in order to give each emissive ion equal weight in the fitting procedure. The rate constant in an individual shell is determined by a luminescence rate in the *absence* of quenchers at the surface (τ_R equal for all shells) and a quenching rate that is dependent on the distance between the (center of the) shell and the particle surface and a quenching constant C. The decay traces were fitted with 10 shells according to Equation 1.

$$I_t = I_0 \sum_{i=1}^{10} \frac{1}{10} e^{-k_i t}; \quad k_i = \frac{1}{\tau_i} = k_R + C f_{q,i}(r) \tag{1}$$

with I_t the intensity at time$=t$, I_0 the intensity at $t=0$, $k_i=1/\tau_i$ the rate constant in shell i, which is the reciprocal of the lifetime in shell i, t the time, k_R the rate constant in the absence of surface quenching (fit parameter), C a quenching constant (fit parameter), and $f_{q,i}(r)$ the quenching factor that takes into account the distance between a shell and the surface with a distance dependence of the quenching proportional to $1/r^6$.[21,22] This function was calculated by integration of the quenching in a shell over the whole surface of the particle. Thus, $f_{q,i}(r)$ is large close to the edge of the particle and much smaller close to the core. Fitting was performed by a least squares method with the "Solver" option in Microsoft Excel.

Fitting gives a τ_R that represents the luminescence lifetime in the absence of surface quenchers and a C that consists of various contributions such as the strength of the quenching and the size distribution of the particles that are not monodisperse. These fit values and the average lifetime (averaged over all subshells) are reported in Table 2. An example of a fitted curve is presented in Figure 4.

The decay curves of the Nd^{3+}-doped particles in methanol with different deuteration grades gave excellent fits with a lifetime τ_R of about 90 µs for all particles and a quenching factor C that decreases with increasing deuteration grade: 3460 s^{-1} in methanol, 639 s^{-1} in methanol-d_1, and 397 s^{-1} in

Table 2. Luminescence lifetimes of LaPO$_4$:Ln.

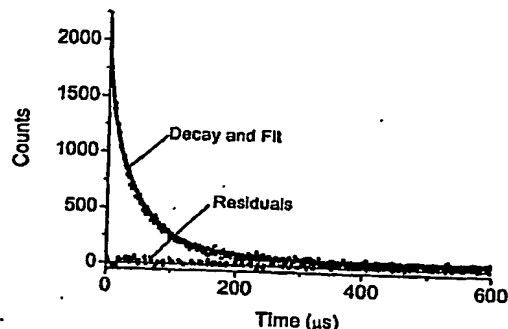| Particle	Medium	$\lambda_{em}/\lambda_{exc}$ [nm]	τ_R [µs]	C [s^{-1}]	τ_{ava} [µs]
LaPO$_4$:Nd	CH$_3$OH	514/880	96	3460	17
LaPO$_4$:Nd	CH$_3$OD	514/880	89	639	39
LaPO$_4$:Nd	CD$_3$OD	514/880	92	397	47
LaPO$_4$:Er (5%)	CD$_3$OD	488/1536	381	10	308
LaPO$_4$:Er (2%)	CD$_3$OD	488/1536	948	5.7	732
LaPO$_4$:Er (1%)	CD$_3$OD	488/1536	1381	3.9	1069
LaPO$_4$:Er (0.5%)	CD$_3$OD	488/1536	2126	2.3	1665
LaPO$_4$:Pr	CD$_3$OD	476/868	8.0	5600	3.8

Fig. 4. Decay of LaPO$_4$:Nd in CH$_3$OD fitted with the model described in the text.

methanol-d_4. The averaged lifetimes (over the whole particle) are: 17 µs, 39 µs, and 47 µs, respectively. The relative decrease in C is much higher upon deuteration of the O–H group than of the C–H group because an O–H group quenches the excited states of lanthanide ions more efficiently than the C–H groups.[22] The effect of the concentration was investigated with Er^{3+}, because its luminescence is very susceptible to processes such as cross relaxation between Er^{3+} ions. In order to study this, the decay of particles with different Er^{3+} concentration was measured, i.e., 5 at.-%, 2 at.-%, 1 at.-%, and 0.5 at.-% of Er^{3+} versus La^{3+}. The decay trace of the particles doped with 5 at.-%, 2 at.-%, 1 at.-%, and 0.5 at.-% Er^{3+} in methanol-d_4 gave excellent fits with $\tau_R = 381$, 948, 1381, and 2126 µs and with 10, 5.7, 3.9, and 2.3 s^{-1} as quenching factor C, respectively. This enhancement in τ_R is due to a reduction in the quenching by Er^{3+} ions (cross-relaxation, self-quenching, and up-conversion). An important factor in the overall quenching is self-quenching, which results in the energy transfer of one excited ion further away from the surface to ions closer to the surface, which are more strongly quenched. This is the reason for the reduction in C with decreasing Er^{3+} concentration. The values for τ_R and C of Pr^{3+} are 8.0 µs and 3600 s^{-1}, respectively, with an average lifetime of 3.8 µs, short compared to the Nd^{3+} and Er^{3+} luminescence, but Pr^{3+} has in general shorter lifetimes due to a large number of possible internal transitions. The luminescence lifetimes found for Nd^{3+} and Er^{3+} are much higher (by up to a factor of 100–1000) than those in solution or in organic complexes.[16a,22] It should be noted that τ_R reported here is not necessarily the natural radiative lifetimes of the lanthanide ions, and quenching

mechanisms other than surface quenching may still be present. The real radiative lifetime of Nd^{3+} is reported to be on the order of 250–400 μs, and that of Er^{3+} on the order of 8000–20 000 μs. A simple calculation shows that the highest luminescence quantum yield ($\phi_{Ln} = \tau_{obs}/\tau_{rad}$) for the La-$PO_4$:Ln particles is about 15 % for both Nd^{3+}- and Er^{3+}-doped particles. In order to have a qualitative measure of the efficiency, the luminescence of the Nd^{3+}-doped particles was compared with the luminescence of $Nd(NO_3)_3$ in methanol-d_4 and in DMSO-d_6. The luminescence lifetimes of that salt in methanol-d_4 and DMSO-d_6 were reported previously by Beeby and Faulkner.[23] These lifetimes and that of $LaPO_4$:Nd and their relative luminescence intensities are reported in Table 3. It can be seen that the (averaged) luminescence lifetime of $LaPO_4$:Nd is enhanced to the same extent as the luminescence intensity. Slight differences are due to variations in the radiative lifetime of Nd^{3+} in the three different environments. So, there is a clear advantage of using $LaPO_4$:Ln.

Table 3. Observed luminescence lifetimes and relative intensities of $Nd(NO_3)_3$ in solution and of $LaPO_4$:Nd.

Nd^{3+}	τ	τ_{rel}	III_{CD_3OD}
CD_3OD	0.48 [a]	1	1
DMSO-d_6	9.02 [a]	19	16
$LaPO_4$:Nd [b]	47	92	98

[a] From ref. [23]. [b] In CD_3OD solution.

As an illustration of the processability, the $LaPO_4$:Nd nanoparticles were incorporated in a polymer matrix on a quartz substrate. A solution of 0.9 g poly(methylmethacrylate) (PMMA) in 5 mL methylethylketone was mixed with a dispersion of 0.1 g of the dry nanoparticles (Nd^{3+}-doped) in 5 mL methanol. Spin coating of this colloidal dispersion on the substrates gave transparent films of about 1 μm thickness. The neodymium ion concentration in this layer is about 10^{19} cm^{-3}. The only difference in the emission spectrum with that taken in CD_3OD solution is caused by absorption of part of the 1.33 μm transition by C–H vibrations in the polymer matrix.

In conclusion, near-infrared emitting lanthanide(III)-doped nanoparticles were successfully made. The particles have good processability and thus the possibility to incorporate them in polymer-based devices. The average luminescence lifetimes of the NIR-emitting lanthanide(III) ions are up to 1.7 ms. These lifetimes make them of particular interest as materials in, e.g., optical amplifiers and laser.

Experimental

Synthesis: Briefly, in this procedure $LaCl_3$ together with the appropriate $LnCl_3$ ($Ln^{3+} = Er^{3+}$, Nd^{3+}, or Pr^{3+}) in 19:1 molar ratio were dissolved in tris-(ethylhexyl)phosphate. This solution was added to a solution containing ortho-phosphoric acid and trioctylamine in tris(ethylhexyl)phosphate and heated to 200 °C for 40 h under exclusion of oxygen and moisture. After cooling down to room temperature, methanol was added to precipitate the doped lanthanum phosphate particles. After precipitation they were collected by centrifugation. To remove all high boiling point organics the residue was stirred twice with methanol and centrifuged again. Finally, the particles were dispersed in methanol by addition of tetramethylammonium hydroxide.

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Near-infrared Emission of Redispersible Er^{3+}, Nd^{3+}, and Ho^{3+} Doped LaF$_3$ Nanoparticles

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ABSTRACT

Nanoparticles of LaF$_3$ doped with Ln^{3+} (Ln = Eu, Er, Nd, and Ho) have been prepared that are dispersible in organic solvents. From the spectrum of Eu^{3+} it has been concluded that the dopant ion occupies a La^{3+} site. The luminescence decays are fitted biexponentially. A given possible explanation for this is a different probability of nonradiative decay for ions at or near the surface and ions in the core of the particles. The lifetimes of Eu^{3+} luminescence at a doping concentration of 5% were 7.7 ± 0.2 and 2.9 ± 0.2 ms, indicative of very high quantum yields. The particles doped with Er^{3+}, Nd^{3+}, and Ho^{3+} are promising materials for polymer-based optical components, because they show luminescence in the telecommunication window (i.e., Er^{3+} at 1530 nm, Nd^{3+} at 1330 nm, and Ho^{3+} at 1450 nm).

Luminescent materials based on lanthanide ions attract a great deal of interest as phosphors in lamps and display devices,[1] components in optical telecommunication,[2] and as the active material in lasers.[3] There is a growing interest to use this luminescence in polymer-based materials, because of easy processing of polymers and ease of integrating different components. The luminescence of the trivalent lanthanide ions arises from transitions within the 4f shell of the ions. These transitions are parity forbidden, leading to low absorption cross-sections and long luminescence lifetimes. However, this long-lived excited state can be quenched very efficiently in the presence of the high-energy vibrations of organic solvents, polymers, or ligands, thus hampering the application in polymer-based devices. Therefore, to use lanthanide luminescence in an organic environment it is important to shield the lanthanide ion from the organic surroundings. Shielding of the lanthanide ion[4] can be achieved by doping it in the inorganic part of nanoparticles, which should still be dispersible in organic solvents. Good dispersibility of the particles is generally achieved by having organic groups on the outside of the particles. Nanoparticles with dimensions of a few nanometers are small enough to minimize Rayleigh scattering in polymer films.[5] Especially the lanthanide ions emitting at wavelengths between 1300 and 1600 nm are of interest for optical telecommunication, because at these wavelengths the silicon-based optical fibers have their maximum transparency.[6]

Most nanoparticles doped with lanthanide ions are made in high-temperature procedures leading to particles without organic groups on the surface and therefore they have no dispersibility in solvents.[7] Only very few examples of these lanthanide-doped nanoparticles have been reported that have a good dispersibility in organic solvents.[8,9] In particular, the near-infrared emitting ions have received little attention.[10]

In this paper we show the synthesis of *lanthanide-doped* LaF$_3$ nanoparticles that have a good dispersibility in organic solvents. LaF$_3$ was chosen as the host matrix because this material has very low vibrational energies,[11] and therefore the quenching of the excited state of the rare earth ions will be minimal. This is especially important for the rare earth ions emitting in the near-infrared part of the spectrum, because they are very sensitive to quenching by high-energy vibrations.[12]

The synthesis of LaF$_3$ nanoparticles was first reported by Dang et al.[13] This procedure was slightly modified to yield luminescent, doped nanoparticles.[14] For the synthesis of the nanoparticles, ammonium di-n-octadecyldithiophosphate was used as the ligand to control particle growth and to stabilize the particles against aggregation. Ammonium di-n-octadecyldithiophosphate was synthesized by heating P$_2$S$_5$ (0.02 mol) and octadecyl alcohol (0.07 mol) at 75 °C for 3 h. The suspension was cooled to room temperature followed by the addition of 50 mL dichloromethane. To remove inorganic salts, the solution was filtered followed by evaporation of the solvent. The remaining residue was taken up in 50 mL of hexane, and ammonia was bubbled through the solution. The precipitate was separated by filtration, washed with hexane, and dried; yield 60%.

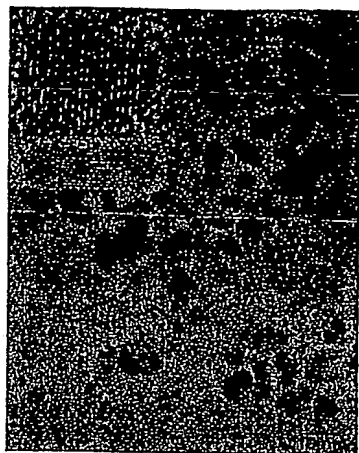* Corresponding author. E-mail: f.c.j.m.vanveggel@ct.utwente.nl

Table 1: Elemental Composition of the Particles

element	wt %	calc. wt %[a]
La[b]	30.96	30.88
Eu[b]	1.61	1.78
P[b]	2.64	2.63
C[c]	35.96	36.82
H[c]	6.63	6.35
N[c]		
S[c]	6.18	5.46

[a] Calculated for 54% ligand and 46% LaF_3 (estimated ratio of La/P from XRF). [b] Determined by XRF. [c] Determined by EA.
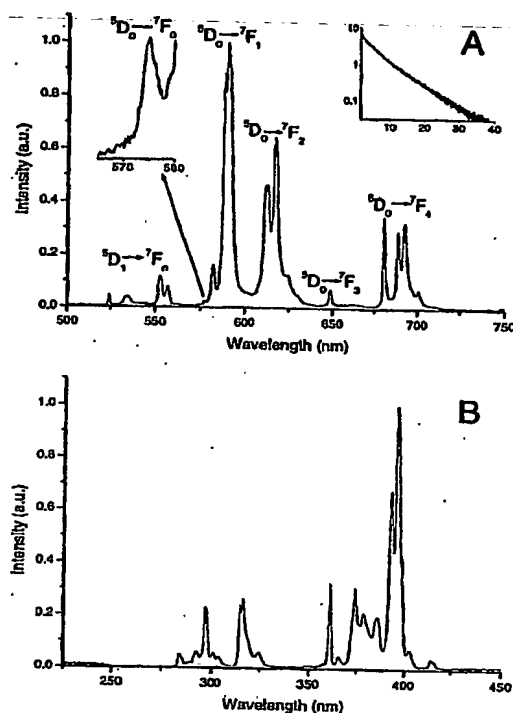

Figure 1. TEM picture of LaF_3/Eu particles. The inset shows the high crystallinity of the particles.

The LaF_3 nanoparticles were prepared by heating a solution of 614 mg (0.95 mmol) ammonium di-*n*-octadecyldithiophosphate and 126 mg (1 mmol) NaF in 35 mL ethanol/water at 75 °C. A solution of $La(NO_3)_3 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ (1.33 mmol total) in 2 mL of water was added dropwise, and the solution was stirred at 75 °C for 2 h and then cooled to room temperature. The precipitate was separated by centrifugation and was washed subsequently with water and ethanol. The particles were further purified by dispersing in dichloromethane and precipitation by the addition of ethanol. After separation by centrifugation the particles were dried in a vacuum over P_2O_5 for 2 days. After drying, the particles can be dispersed in apolar solvents such as chloroform, dichloromethane, and toluene.

First, the characterization of particles doped with Eu^{3+} is described, because this ion is a good probe for the chemical environment of the lanthanide ion. The same procedure was used to make LaF_3 nanoparticles doped with Er^{3+}, Nd^{3+}, and Ho^{3+}, which have transitions in the near-infrared at wavelengths interesting for optical telecommunication.

The particles of LaF_3 doped with 5% Eu^{3+} were characterized by TEM by evaporating a drop of the particle dispersion in CH_2Cl_2 on a carbon coated TEM grid (Figure 1).

The particles are single crystals but not ideally spherical, with diameters between 5 and 10 nm. These sizes are small enough to minimize Rayleigh scattering. In the higher magnification inset the high crystallinity of the particles can clearly be seen. The crystal lattice plains can be seen in the spherical and in the elongated particles, so the elongated particles are not formed by aggregates of smaller particles. The elemental composition of the particles was determined by X-ray fluorescence (XRF) and combustion elemental analysis (EA). The results are summarized in Table 1.

The XRF analysis confirms that the same ratio of Eu/La is present in the particles as applied in the synthesis. Combustion elemental analysis confirms the absence of free ligand, because no nitrogen of the ligand counterion was detected. Fluorine cannot be detected with both of these methods.

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Figure 2. (A) Emission (λ_{ex} 397 nm) and (B) excitation (λ_{em} 591 nm) spectrum of LaF_3:Eu particles dispersed in CH_2Cl_2 with a Eu^{3+} concentration of $\sim10^{-3}$ M. Steady-state measurements were done with an Edinburgh Instruments FS/FL900 instrument with a 450 W Xe arc lamp as excitation source and a red sensitive, Peltier element cooled Hamamatsu R955 PMT. The emission spectrum was corrected for the detector response, and the excitation spectrum was corrected for the lamp intensity. The left inset shows a high-resolution (0.09 nm) spectrum of the peak of the $^5D_0 \rightarrow ^7F_0$ transition at 578 nm. The right inset shows the luminescence decay of the $^5D_0$ level at 591 nm (λ_{ex} 397 nm) measured by exciting the sample with a microsecond flashlamp.

The room-temperature emission and excitation spectra of LaF_3 doped with 5% Eu^{3+} are shown in Figure 2.

In the emission spectrum the characteristic Eu^{3+} transitions can be seen from the $^5D_1$ and $^5D_0$ level. All Eu^{3+} ions are in the same crystal site, because only one peak for the $^5D_0 \rightarrow ^7F_0$ transition is observed at 578 nm. These two energy levels are nondegenerate, so one peak will be observed when all Eu^{3+} ions are in the same environment. The symmetry of the crystal site in which the Eu^{3+} ions are located is

Table 2: Luminescent Lifetimes of LaF₃/Eu Particles in Different Solvents[a]

solvent	r^p	τ_1	τ_2
ethyl ether	1.352	9.5 (67%)	3.6 (33%)
pentane	1.357	8.4 (77%)	2.9 (23%)
hexane	1.375	8.2 (76%)	2.9 (24%)
THF	1.407	8.1 (73%)	3.0 (27%)
dichloromethane	1.424	7.7 (74%)	2.9 (26%)
chloroform	1.446	7.4 (75%)	2.8 (25%)
toluene	1.497	6.8 (72%)	2.7 (25%)
chlorobenzene	1.525	6.8 (72%)	2.8 (28%)

[a] The percentages reflect the amount of the component contributing to the total lifetime.

Table 3: Luminescent Lifetimes of LaF₃/Eu in CH_2Cl_2 at Different Eu^{3+} Doping Concentrations[a]

Eu^{3+} conc.	τ_1 (ms)	%	τ_2 (ms)	%
1%	9.1 ± 0.2	87 ± 5	2.8 ± 0.2	13 ± 5
2%	8.5 ± 0.2	83 ± 5	2.7 ± 0.2	17 ± 5
5%	7.7 ± 0.2	74 ± 5	2.9 ± 0.2	26 ± 5

[a] λ_{ex} 397 nm, λ_{em} 591 nm. The percentages reflect the amount of the component contributing to the total lifetime. The errors are determined from duplicate measurements.

determined by the ratio of the $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_2$ transitions. The $^5D_0 \to {}^7F_2$ transition is hypersensitive, but the $^5D_0 \to {}^7F_1$ transition is insensitive to the environment and the ratio of the two intensities is a good measure for the symmetry of the Eu^{3+} site. In a site with inversion symmetry the $^5D_0 \to {}^7F_1$ magnetic dipole transition is dominating, while in a site without inversion symmetry the $^5D_0 \to {}^7F_2$ electric dipole transition is the strongest.[15] The calculated intensity ratio is 0.95, which is in good agreement with C_2 symmetry, similar to that of the La^{3+} ion in bulk LaF_3.[16] The peak intensities are similar to those found for bulk LaF_3 [17] doped with Eu^{3+}, fully consistent with the incorporation of the Eu^{3+} ion inside the LaF_3 nanoparticle. In the excitation spectrum the characteristic absorption bands of Eu^{3+} can be seen.

The inset of Figure 2 shows the luminescence decay of the 591 nm emission, when Eu^{3+} was excited directly at 397 nm. The luminescence decay of the $^5D_0$ level is clearly not monoexponential, and a good fit was obtained with two exponentials. The fitted values for the lifetimes are 7.7 ± 0.2 ms (74%) for the long component and 2.9 ± 0.2 ms (26%) for the short component. The value is slightly higher than the radiative lifetime of 6.9 ms calculated before for Eu^{3+} in bulk LaF_3.[17b] It is more often observed that the luminescence lifetime of nanocrystalline material is somewhat higher than for the bulk material,[18] which can be explained by a different refractive index of the medium around the particles. When we look at the luminescence lifetime of our particles in solvents with different refractive index we see the same as was previously found.[19] The results are summarized in Table 2.

An increase in refractive index leads to a decrease in luminescence lifetime, while no difference in the luminescence spectrum was observed. The decays are still biexponential and the effect of the medium is primarily seen on the long component of the lifetime. There are a number of possible explanations for the multiexponential decay of the luminescence. One possible explanation is a different probability of nonradiative decay for ions at or near the surface and ions in the core of the particles. The LaF_3 matrix has very low phonon energies ($\sim$350 cm^{-1}),[20] so quenching from the host is negligible. The ions on the outside of the particles are more susceptible to the high energy vibrations of the ligand at the surface. There is also a small amount of water, which is a known quencher, adsorbed to the surface of the

particles. This was confirmed by performing the synthesis of the particles in D_2O/EtOD solvent. An increase in the two components of the lifetime was observed to 9.0 ms (65%) and 4.0 ms (35%). When this product was stirred in a mixture of water/ethanol, the values of the lifetime were back to the values observed for particles synthesized in nondeuterated solvent. This experiment confirms the presence of water, which is accessible to solvent and therefore not inside the crystal lattice, but at the surface of the particles. This surface interaction would also lead to different lifetimes for different sizes of particles, because smaller particles have a larger surface-to-volume ratio than the larger particles. The size and size distribution is therefore an important factor influencing the luminescence lifetime. A second possibility for biexponential decay is that the doping ions are not homogeneously spread over the particles, leading to variations in local doping concentrations. At this moment we do not have any information about the distribution of the ions in the particles; however, the Eu^{3+} ions are located at a La^{3+} site so a statistical distribution is expected. To investigate the concentration quenching effect, particles doped with different concentrations of Eu^{3+} were synthesized. The measured luminescence lifetimes are also summarized in Table 3.

As can be seen, the lifetime of the $^5D_0$ level is dependent on the dopant concentration, but the decays are still biexponential. By decreasing the Eu^{3+} concentration the average distances between the ions is increased, leading to a less efficient transfer of energy between the ions. The concentration dependence of the lifetime suggests that energy transfer from one Eu^{3+} ion to the other is important in the quenching of the excited state. A mechanism consistent with these findings is the energy migration over the Eu^{3+} ions until a quenching site is reached.[21] This quenching site is probably located at the surface, and at low concentrations it will be reached less efficiently, leading to longer luminescent lifetimes.

The same procedure was used to dope LaF_3 particles with lanthanide ions that show emission in the near-infrared. Doping concentrations of 5% were applied of Er^{3+}, Nd^{3+}, and Ho^{3+}, and the emission spectra were measured.

In the emission spectra of Figure 3 the luminescence of LaF_3 nanoparticles doped with Er^{3+}, Nd^{3+}, and Ho^{3+} is observed. The emissions of these ions cover the complete telecommunication window between 1300 and 1600 nm. The Er^{3+} signal at 1530 nm ($^4I_{13/2} \to {}^4I_{15/2}$) shows a wide bandwidth with a full width at half-maximum (fwhm) of about 70 nm comparable to the fwhm measured before on a LaF_3:Er film.[22] The luminescence decay was fitted with one exponential,
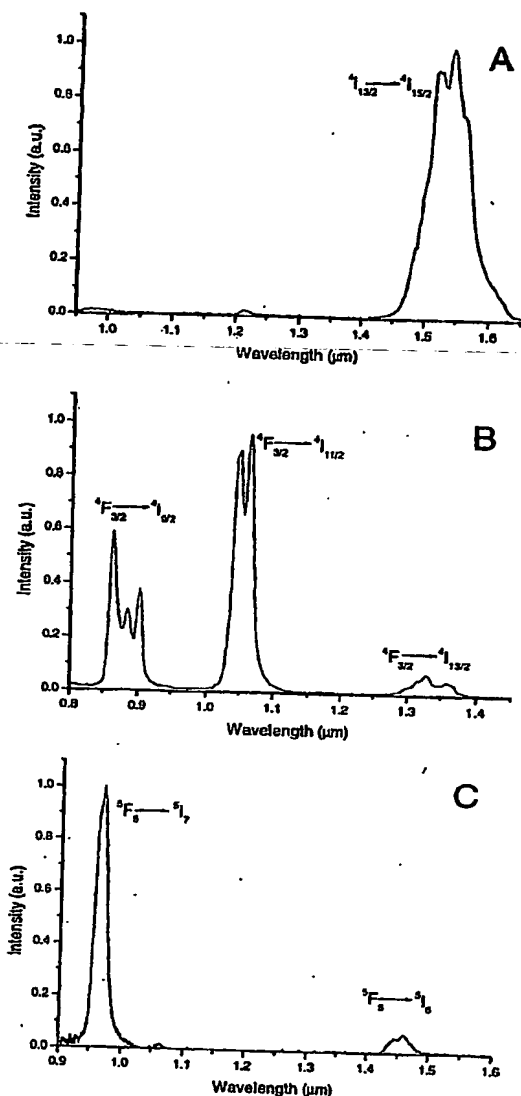
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shows the typical luminescence of Nd^{3+} at 880, 1060, and 1330 nm ($^4F_{3/2}\rightarrow^4I_J$, $J = 9/2$, 11/2, and 13/2, respectively). The measured lifetimes of the $^4F_{3/2}$ level when fitted with two exponentials were 240 μs (77%) and 40 μs (23%). The spectrum of LaF_3:Ho shows emissions centered at 966 nm ($^5F_5\rightarrow^5I_7$) and 1460 ($^5F_5\rightarrow^5I_6$) nm with lifetimes of 340 μs (6%) and 30 μs (94%) when fitted with two exponentials. In the visible also the emission of the $^5F_5\rightarrow^5I_8$ at 640 nm was observed (not shown).

In conclusion, Ln^{3+}-doped nanoparticles of LaF_3 have been synthesized that are dispersible in organic solvents. The particles can be produced in a simple procedure with high yields, and the dopant type and concentration can easily be varied for different applications. Especially the ions emitting in the near-infrared are of interest for telecommunication purposes, and we are investigating the use of this material in polymer-based optical amplifiers. The dopant ion is located in the La^{3+} crystal site inside the particles leading to long luminescent lifetimes in organic solvent. The luminescence decay generally shows a biexponential decay, probably due to surface effects. A way to improve the luminescence of ions located at or near the surface might be to grow a layer of undoped LaF_3 around the particles.

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Figure 3. Emission spectra of (A) LaF_3/Er and (B) LaF_3/Nd measured by exciting the samples with a CW Ar+ ion laser operating at 488 nm (Er^{3+}) and 514 nm (Nd^{3+}). The continuous light was modulated with an acoustic optic modulator and focused on the sample in 1 × 1 cm quartz cuvettes (concentration 10^{-3} M). The signal was focused with a 20 cm lens on a monochromator and detected at the monochromator exit with a liquid nitrogen cooled Ge detector (Northcoast) or a PMT (AgOCS) for the spectral region between 700 and 1000 nm. The signal of the detectors was fed to a lock-in amplifier. The spectrum of (C) LaF_3/Ho was measured using an Edinburgh Instruments FS/FL900 instrument, exciting the sample at 448 nm with an a 450 W Xe arc lamp and by collecting the emission with a nitrogen-cooled Ge detector.

and a lifetime of 220 μs was obtained. A possible explanation for the monoexponential decay is that the ions are located closer to the surface due to a stronger ligand–Er interaction and therefore are built in the particles at a later stadium of particle formation. Due to stronger quenching, this might lead to a monoexponential decay. The spectrum of LaF_3:Nd

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